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205EF03 E859766-1 072662
F01/7700 0.00-0322483.9

2.	Patent application number *(The Patent Office will fill in this part)*	**0322483.9**

3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	THERMO FINNIGAN LLC 355 RIVER OAKS PARKWAY SAN JOSE CALIFORNIA 95134-1991 UNITED STATES OF AMERICA
	Patents ADP number *(if you know it)*	812581700/
	If the applicant is a corporate body, give the country/state of its incorporation	DELAWARE, UNITED STATESOF AMERICA

4.	Title of the invention	MEASURING CELL FOR ION CYCLOTRON RESONANCE SPECTROMETER

5.	Name of your agent *(if you have one)*	BOULT WADE TENNANT
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	VERULAM GARDENS 70 GRAY'S INN ROAD LONDON WC1X 8BT
	Patents ADP number *(if you know it)*	42001

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7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing *(day / month / year)*

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Description	**12**
Claim(s)	**5**
Abstract	**0**
Drawing(s)	**6**

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Priority documents

Translations of priority documents

Statement of inventorship and right
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Request for preliminary examination
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Request for substantive examination
(Patents Form 10/77)

Any other documents
(Please specify)

11 · I/We request the grant of a patent on the basis of this application.

Signature

Date

25 September 2003

12. Name and daytime telephone number of person to   **Dr. Alex Frost**
contact in the United Kingdom   **020 7430 7500**

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MEASURING CELL FOR ION CYCLOTRON RESONANCE SPECTROMETER

This invention relates to a measuring cell for an
Ion Cyclotron Resonance (ICR) spectrometer.

5   Fourier Transform Ion Cyclotron Resonance is a
technique for high resolution mass spectrometry which
employs a cyclotron principle.

One such FT-ICR spectrometer is shown in our
co-pending Application No. GB 0305420.2 which is
10   incorporated herein by reference in its entirety. As is
described in that application, ions generated in an ion
source (usually at atmospheric pressure) are transmitted
through a system of ion optics employing differential
pumping and into an ion trap. Ions are ejected from the
15   trap, through various ion guides and into a measurement
cell. In that cell, the field lines of a homogeneous
magnetic field (generated by an external superconducting
magnet, for example), extend along the cell in parallel
with the cell's longitudinal axis. By applying an r.f.
20   field, perpendicular to the magnetic field, the ions can
be excited so as to produce cyclotron resonance. Charged
particles in the cell then orbit as coherent bunches
along the same radial paths but at different frequencies.
The frequency of the circular motion (the cyclotron
25   frequency) is proportional to the ion mass. A set of
detector electrodes are provided and an image current is
induced in these by the coherent orbiting ions. The
amplitude and frequency of the detected signal are
indicative of the quantity and mass of the ions. A mass
30   spectrum is obtainable by carrying out a Fourier

Transform of the 'transient', i.e. the signal produced at the detector's electrodes.

Figure 1a shows, highly schematically, the arrangement of electrodes in a prior art cell. In particular, a section through a cell 10 is shown, along with its longitudinal axis z. An orthogonal section through the cell 10 is also shown in Figures 1d and 1e which show, respectively, the electrode arrangements in a cylindrical and in a square rectangular configuration respectively..

In Figure 1a, the cell 10 comprises a central electrode 20 and outer electrodes 30, 40 surrounding that. An r.f. voltage is applied to each of the electrodes so as to produce an excitation field, and a d.c. voltage is applied to the outer electrodes 30, 40 so as to provide a trapping field.

The trapping field created by the prior art arrangement of Figure 1a is shown in Figure 1b.

The longitudinal ("z") axis of Figure 1b is intended to be generally to the same scale as that of Figure 1a, so that the magnitude of the trapping field U in the z-direction of Figure 1b corresponds with the position along the z axis of the electrodes in Figure 1a. Figure 1b also shows the approximate range of the homogeneous field region of the applied magnetic field.

Figure 1c shows a schematic representation of equipotentials of the excitation field in the cell 10 of Figure 1a. It will be seen that the excitation field equipotentials are generally parallel to the z axis in the centre of the cell and close to the 'z' axis, so that there is no excitation electric field component in the z

direction, but curve significantly so that there is a non-zero excitation electric field component in the z-direction (see Figure 1g). Optimal excitation for FTMS requires an homogeneous electrical excitation field. R.f.

5   electric field components in the radial direction of the cell cause the ions to gain energy in that (desired) radial direction. Any finite electrical excitation field component in the direction of the cell's longitudinal axis 'z' causes an acceleration in that axial direction.

10   Longitudinal acceleration of ions is undesirable because the potential barrier in that direction is typically only of order 1 eV (higher trapping potentials causing unwanted field distortion) and so ions may easily escape from the cell and thus be lost.

15   One theoretical possibility to remove the axial r.f. field components towards the edges of the cell would be to make the electrodes of infinite length. The problem with this is that, as the electrodes become longer in the z-direction, so the ions reside in a volume that extends

20   outside of the homogeneous zone of the magnetic field. This in turn causes a reduction in the resolving power of the spectrometer.

An alternative approach to the production of an excitation electric field with parallel field lines is

25   described in US-A-5,019,706. Here, additional electric r.f. signals are applied to one or more of the trapping electrodes on both sides of the measuring cell. This causes the inhomogeneities in the field lines at the cell extremities (as a result of its finite length in the

30   axial direction) to be balanced out by heterodyning with the additional r.f. field components which are introduced

by the trapping electrodes, so that the ions in the trap experience an r.f. field more like that which would be produced by a cell of infinite axial length. Lines of equipotential in the cell of US-A-5,019,706 are shown for

5 the purposes of illustration only, in Figure 1f.

Nevertheless, the arrangement of US-A-5,019,706 suffers from the disadvantage that electrodes have to share the static trapping potential and the RF excitation potentials, which may increase the cost of the driving

10 electronics and/or the amount of noise. Furthermore, the potential well which traps ions in the cell extends as far as the region of excitation field curvature in this arrangement so that trapped ions still experience an inhomogeneous excitation field, as may be seen from

15 Figure 1f.

Against this background, there is provided, in a first aspect, a measurement cell for an FTMS spectrometer, comprising: a plurality of excitation electrodes arranged symmetrically about a longitudinal

20 axis which extends in a direction generally parallel to the field direction of an applied homogeneous magnetic field; and a plurality of trapping electrodes, also arranged symmetrically about the said longitudinal axis; wherein at least some of the excitation electrodes are

25 arranged axially outwardly of the trapping electrodes.

Placing at least some of the excitation electrodes axially outwardly of the trapping electrodes causes the non-linear region of the excitation field to be "pulled" axially outwards relative to the prior art arrangements

30 so that the field lines are more linear in the region axially between the trapping electrodes in which the ions

are confined and where, in preference, the magnetic field is homogeneous.

In accordance with a further aspect of the present invention, there is provided a method of trapping and exciting ions in a measurement cell of an FTMS spectrometer, the method comprising: (a) applying a magnetic field to the measurement cell so as to produce a region of homogeneous magnetic field, having a magnetic field direction, within the cell; (b) applying a d.c. trapping potential to a plurality of trapping electrodes which are arranged symmetrically about a longitudinal axis which extends in a direction generally parallel to that magnetic field direction, so as to trap ions in the cell, in that axial direction; and (c) applying an r.f. excitation potential to a plurality of excitation electrodes which are arranged symmetrically about that longitudinal axis, so as to resonantly excite the ions in the cell, at least some of the excitation electrodes being arranged axially outwardly of the trapping electrodes; wherein the ions are trapped within the region of homogeneous magnetic field and wherein the ions are further trapped within a homogeneous region of an excitation electric field generated by the application of the r.f. excitation potential to the said excitation electrodes.

Further preferred features are set out in the dependent claims which are appended hereto.

The invention may be put into practice in a number of ways and some preferred embodiments will now be described by way of example only and with reference to the accompanying drawings, in which:

Figure 1a shows a schematic longitudinal section through a prior art FTMS measurement cell;

Figure 1b shows, to the same scale as Figure 1a, the d.c. trapping potential U along the longitudinal axis z of the cell of Figure 1a;

Figure 1c shows, again to the same scale as Figure 1a, lines of r.f. excitation equipotential τ along the longitudinal axis z of the cell of Figure 1a;

Figures 1d and 1e show views along the line AA of Figure 1a, for circular and square section cells respectively;

Figure 1f shows lines of r.f. excitation potential τ along the longitudinal axis of the measurement cell of US-A-5,019,706 which also forms a part of the state of the art;

Figure 1g shows the electrical field components of an arbitrary point on an r.f. excitation field equipotential of the cell of Figure 1a, towards the edges of that cell, along with an indication of the radial and axial components of force thereby applied to an ion at that point;

Figure 2a shows a schematic longitudinal section through an FTMS measurement cell in accordance with a first embodiment of the present invention;

Figure 2b shows, to the same scale as Figure 2a, the d.c. trapping potential U along the longitudinal axis z of the cell of Figure 2a;

Figure 2c shows, also to the same scale as Figure 2a, lines of equipotential for the r.f. excitation field τ along the longitudinal axis z of the cell of Figure 2a;

Figure 3a shows a schematic longitudinal section through an FTMS measurement cell in accordance with a second embodiment of the present invention;

Figure 3b shows, to the same scale as Figure 3a,
5   lines of equipotential for the r.f. excitation field τ along the longitudinal axis of the measurement cell of Figure 3a;   and

Figure 4 shows a schematic longitudinal section through an FTMS measurement cell in accordance with a
10   third embodiment of the present invention.

Turning first to Figure 2a, a schematic longitudinal section through an FTMS measurement cell 100 in accordance with a first embodiment of the present invention is shown. The cell 100 is rotationally
15   symmetrical about a longitudinal axis z and may, for example, be cylindrical or oblong in shape, as will be explained further below.

The cell 100 comprises a first pair of central excitation electrodes 110 which are located about an
20   axially central point of the cell 100. Axially outward of this central pair of excitation electrodes 110, on either side thereof, are two pairs of trapping electrodes 120, 130. The trapping electrodes of Figure 2a have the same, or similar, diameter, to the first pair of excitation
25   electrodes 110.

Axially outwardly of the pairs of trapping electrodes 120, 130 are second and third pairs of outer excitation electrodes 140, 150 respectively. Again, the diameter of these outer excitation electrode pairs is the
30   same or similar to that of the trapping and central excitation electrode pairs. Thus, the outer electrode

pair 140 and the central electrode pair 110 'sandwich'
the trapping electrode pair 120 between them, and the
outer electrode pair 150 and central electrode pair 110
'sandwich' the trapping electrode pair 130 between them.

5   An r.f. voltage supply 160 is connected, in the
embodiment of Figure 2a, to each of the excitation
electrode pairs 110, 140, 150. Although a single r.f.
voltage supply (of a given voltage) may be attached to
ach of the excitation electrode pairs, different voltages
10   and/or frequencies may instead be applied to each by
virtue of voltage and/or frequency divider(s)
respectively, or by using separate r.f. voltage supplies.

       A d.c. voltage 170 is applied to the trapping
electrodes 120, 130. Again, the same or different d.c.
15   voltages may be applied to the two pairs of trapping
electrodes 120, 130.

       Figure 2b shows a schematic plot of the trapping
field, U, as a function of axial position z. It will be
seen that, in comparison with the prior art arrangement
20   of Figure 1b, the trapping field has two clearly defined
peaks 180 which coincide with the axial positions of the
trapping electrodes 120, 130. The peaks then tail off
sharply as the position z moves further away from the
centre of the cell 100.

25   Figure 2c shows a schematic of the lines of
equipotential of the excitation field generated in the
cell 100 of Figure 2. It will be noted that the field
lines are relatively flat and parallel with the z axis,
across the bulk of the region of confinement of the ions
30   which is between the two peaks 180 of the trapping
potential U (Figure 2b). There is a small perturbation

190 in the excitation field in the region of the trapping electrodes, as is seen in Figure 2c, but this has not been found to affect the overall trapping and excitation unduly.

5   The arrangement of Figure 2a accordingly "pulls" the non-linear region of the excitation field outwards relative to the arrangement of Figure 1a so that the excitation electric field is essentially homogeneous in the trapping region. It will also be noted that the axial

10   barriers formed by the peaks 180 in the trapping field coincide with the homogeneous area of the magnetic field (cf US-A-5,019,706, described above, where the (physical) axial barriers for trapped ions are in that case outside the homogeneous area of the magnetic field). Thus, high

15   resolution FTMS measurements can be made (because a large proportion of trapped ions experience homogeneous magnetic and excitation fields) whilst the number of ions lost after injection into the cell 100 is minimized.

       Although not shown in the Figures, it will be

20   understood that the cell 100 of Figure 2 also includes detecting electrodes which may (as in the arrangements of Figure 1d or 1e) be radially interspersed with the trapping and excitation electrodes. It is advantageous to have the detecting electrodes and the trapping/excitation

25   electrodes radially equally spaced from the axis z so as to retain symmetry.

       Figure 3a shows an alternative arrangement of a measurement cell 100' to that of Figure 2a. Features common to these two Figures are nevertheless labelled

30   with like reference numerals. In the cell 100' of Figure 3a, instead of connecting the r.f. voltage supply 160

only to the excitation electrodes 110, 140, 150, it is
also connected, along with the d.c. voltage 170 to the
trapping electrodes 120, 130. The logical layout of
electrode potentials is shown in the upper part of Figure
5   3a. The physical layout, indicating one way of wiring the
electrodes is shown in the lower part of that Figure. It
will be seen that the r.f. and d.c. voltage supplies 160,
170 are decoupled from one another by employing a
capacitance 200 between the r.f. and d.c. supplies to the
10 trapping electrodes 120, 140, so that d.c. is not also
supplied via the r.f. electrical leads to the excitation
electrodes 110, 140, 150. Applying a combined d.c. and
r.f. field in this way reduces the presence of the
perturbation 190 in the vicinity of the trapping
15 electrodes, as may be seen from Figure 3b which shows
lines of equipotential in the cell 100' of Figure 3a.

　　　Turning finally to Figure 4, a further embodiment of
a cell 100" for FTMS is shown. Again, the components
common to Figures 2a, 3a and 4 are labelled with like
20 reference numerals. In the arrangement of Figure 4, each
of the electrodes 110, 120, 130, 140 and 150 is
selectively connectable to a.c. and d.c. voltages which
are decoupled using capacitances 200. This allows for
maximum flexibility. For example, each of the electrodes
25 can first be energized with d.c. only, when the cell is
first filled with ions. Thus, a trapping field can be
established which has boundaries extending right to the
edges of the cell 100". This trapping field can then be
adjusted so as to squeeze the ions towards the centre of
30 the cell 100"; in particular, the d.c. voltage can be
adjusted on the electrodes so as to shift the potential

well towards the centre of the cell 100″ until there is
no more d.c. voltage on the outer excitation electrodes
140, 150 or on the central excitation electrodes 110, and
the trapping field resembles that of Figure 2b. At that
5   point, the r.f. voltage supply 160 can be applied to the
excitation electrodes 110, 140, 150 to arrive at the
configuration of Figure 2a, or it may be applied to all
of the electrodes, excitation plus trapping, to arrive at
the configuration of Figure 3a. Other static field
10 configurations may be envisaged as a precursor to the
preferred trapping/excitation arrangements.

     Although some specific embodiments of the invention
have been described, it will be understood that these are
by way of example only and that various modifications are
15 possible. For example, whilst in Figures 3a and 4, the
r.f. and d.c. voltages are decoupled using a capacitance,
an inductance may be employed instead or as well.
Furthermore, although only two pairs of outer excitation
electrodes have been described, additional outer
20 excitation electrodes may be employed, so as further to
reduce inhomogeneities in the excitation field in the
region of the homogeneous magnetic field. Indeed,
interlaced trapping/excitation/trapping/excitation
arrangements may also be employed.

25   As a further refinement, the cell 100, 100′ and 100″
may be fitted with end caps (not shown) that are located
at either end of the cell, adjacent the outer excitation
electrode pairs 140, 150 and which are mounted coaxially
with the electrodes. Preferably, these end caps have a
30 radius somewhat less than that of the excitation and
trapping electrodes so that the cell is only partially

physically closed by the end caps. This arrangement permits the field shape to be controlled still further.

As still a further alternative, the central excitation electrode pair 110 may have a different

5   diameter and/or may not be coaxial with the adjacent trapping electrode pairs 120, 130 or the outer excitation electrodes 140, 150. This allows for compensation for the excitation field in the vicinity of the trapping electrodes, once again so as to remove or at least reduce

10 the magnitude of the perturbation 190 (Figure 2c).

CLAIMS:

1.   A measurement cell for an FTMS spectrometer,
comprising:

a plurality of excitation electrodes arranged
symmetrically about a longitudinal axis which extends in
a direction generally parallel to the field direction of
an applied homogeneous magnetic field; and

a plurality of trapping electrodes, also arranged
symmetrically about the said longitudinal axis;

wherein at least some of the excitation electrodes
are arranged axially outwardly of the trapping
electrodes.

2.   The measurement cell of claim 1, wherein the
plurality of excitation electrodes comprises a central
electrode set, arranged about a central point along the
longitudinal axis, and first and second outer electrode
sets, axially spaced from the central electrode set along
that axis, and wherein the trapping electrodes comprise
first and second trapping electrode sets, located axially
between the outer electrode set and the first and second
outer electrode sets of the excitation electrodes
respectively.

3.   The measurement cell of claim 1 or claim 2,
further comprising an r.f. voltage supply connected to
the plurality of excitation electrode, and a d.c. voltage
supply connected to the plurality of trapping electrodes.

4.   The measurement cell of claim 3, wherein the r.f. voltage supply is further connected to the plurality of trapping electrodes.

5   5.   The measurement cell of claim 4, wherein the r.f. voltage supply and the d.c. voltage supply are decoupled.

6.   The measurement cell of claim 5, wherein the 10 r.f. voltage supply is capacitively and/or inductively coupled to the trapping electrodes.

7.   The measurement cell of any one of the preceding claims, wherein the excitation electrodes and 15 the trapping electrodes are each equidistantly spaced about the longitudinal axis of the measurement cell.

8.   The measurement cell of any one of claims 1 to 6, wherein at least one of the excitation electrodes is 20 radially spaced from the longitudinal axis at a first distance which is different to that of the or each of the other excitation electrodes.

9.   The measurement cell of claim 2, wherein the 25 central electrode set is radially spaced from the longitudinal axis at a first distance which is different to that of the first and second trapping electrode sets and also different to that of the first and second outer electrode sets.

30

10. The measurement cell of any one of the preceding claims, further comprising end caps arranged axially outwardly of the trapping and excitation electrodes.

5

11. The measurement cell of claim 10, wherein the end caps are located along the longitudinal axis of the cell so as partially to enclose a volume therebetween.

10   12. The measurement cell of any preceding claim, wherein the plurality of excitation electrodes comprises:

a first pair of curved excitation electrodes arranged symmetrically about the longitudinal axis of the cell and about a central point along that longitudinal
15 axis;

second and third pairs of curved excitation electrodes each arranged symmetrically about the longitudinal axis of the cell, and equidistantly spaced along that axis about the central point thereof; and

20   first and second pairs of curved trapping electrodes, arranged symmetrically about the longitudinal axis, each trapping pair being arranged between the first pair of curved excitation electrodes and the second and third pairs of curved excitation electrodes respectively;

25   the cell further comprising a pair of detection electrodes radially spaced about the longitudinal axis of the cell with respect to the excitation and trapping electrodes, and having a diameter similar to the said excitation and trapping electrodes.

30

13. A Fourier Transform Mass Spectrometer including the measurement cell of any of claims 1-12.

14. A method of trapping and exciting ions in a
5 measurement cell of an FTMS spectrometer, the method comprising:

(a) applying a magnetic field to the measurement cell so as to produce a region of homogeneous magnetic field, having a magnetic field direction, within the
10 cell;

(b) applying a d.c. trapping potential to a plurality of trapping electrodes which are arranged symmetrically about a longitudinal axis which extends in a direction generally parallel to that magnetic field
15 direction, so as to trap ions in the cell, in that axial direction; and

(c) applying an r.f. excitation potential to a plurality of excitation electrodes which are arranged symmetrically about that longitudinal axis, so as to
20 resonantly excite the ions in the cell, at least some of the excitation electrodes being arranged axially outwardly of the trapping electrodes;

wherein the ions are trapped within the region of homogeneous magnetic field and wherein the ions are
25 further trapped within a homogeneous region of an excitation electric field generated by the application of the r.f. excitation potential to the said excitation electrodes.

30   15. The method of claim 14, further comprising:

applying an r.f. excitation potential to at least one of the plurality of trapping electrodes in addition to the d.c. trapping potential applied thereto.

5   16.   The method of claim 15, further comprising applying the r.f. excitation potential to each of the trapping electrodes along with the d.c. trapping voltage applied thereto.

10   17.   The method of claim15 or claim 16, wherein the step of applying the r.f. excitation potential to the or each of the trapping electrodes comprises coupling the r.f. excitation potential to the or each trapping electrode via a capacitance and/or an inductance.

15

   18.   The method of claim14 or claim 15 or claim 16, further comprising, prior to at least one of the steps (a), (b) and (c):
      applying a d.c. trapping potential to one or more of
20   the excitation electrodes so as to generate a first ion trapping field; and
      subsequently removing the said d.c. trapping potential from the excitation electrodes to which it has been applied.

25

30   184238

Prior Art

10 stage

DC A ← DC ~RF

30   20   40

Z

DC A DC ~RF
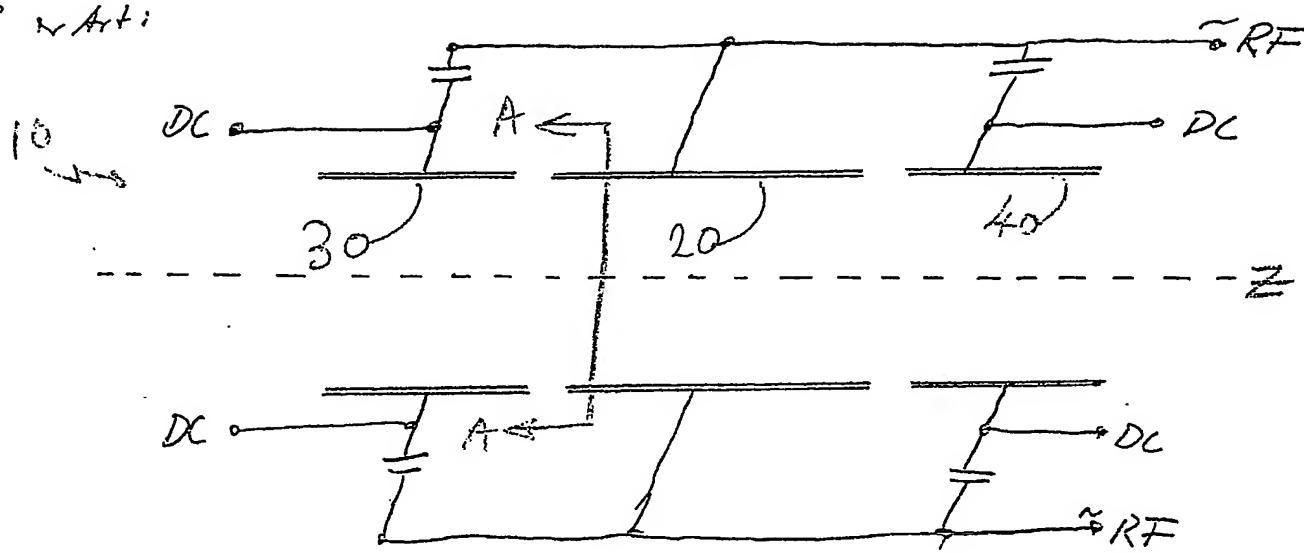
Fig. 1a
PRIOR ART

Storage Field:

U

$\vec{B}$ homogeneous

O

q
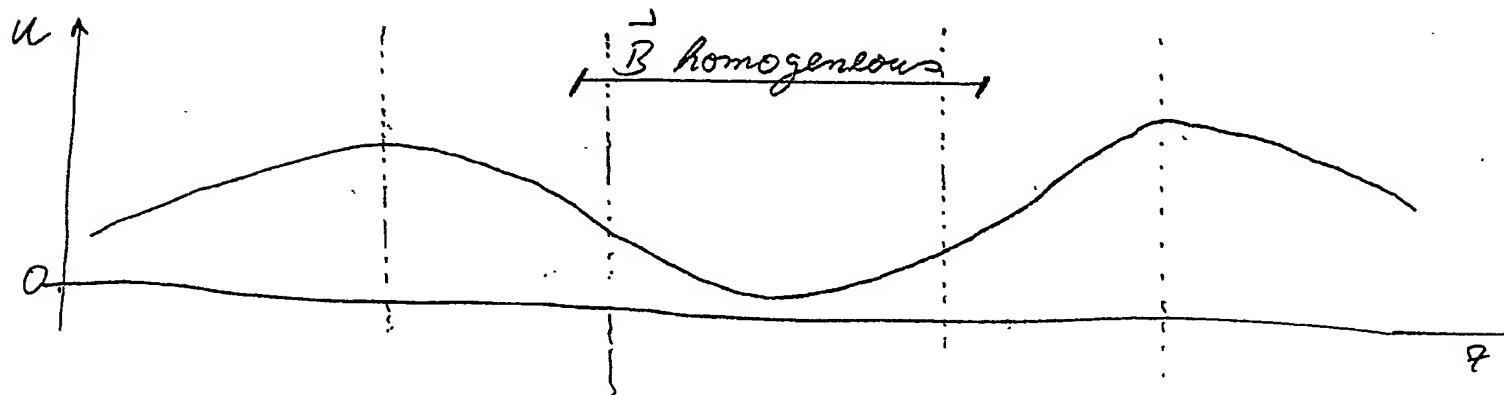
Fig. 1b
PRIOR ART

Side View:
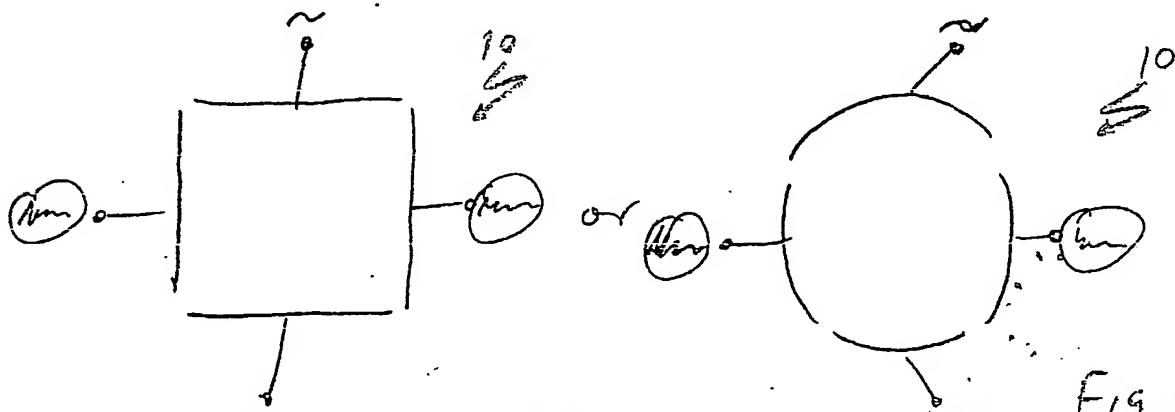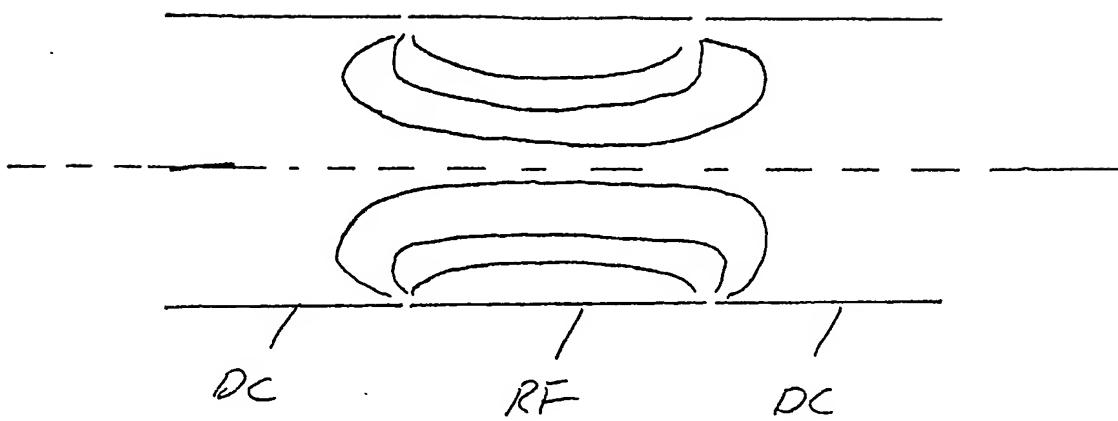
~ 10

~ 10

or

Fig. 1d
Fig. 1e
PRIOR ART

DC RF DC

FIG 1c

PRIOR ART.

Prior Art: Excite field ; isopotential lines

region of ion confinement
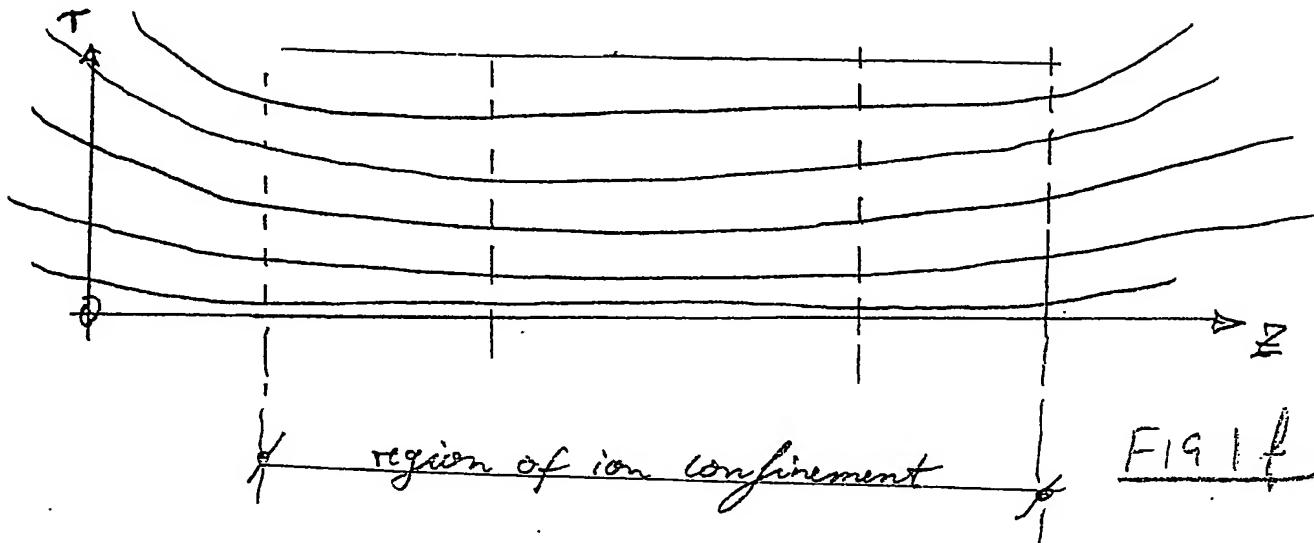
FIG 1f

Field curvature and Force $\vec{F}$; Field $\vec{E}$
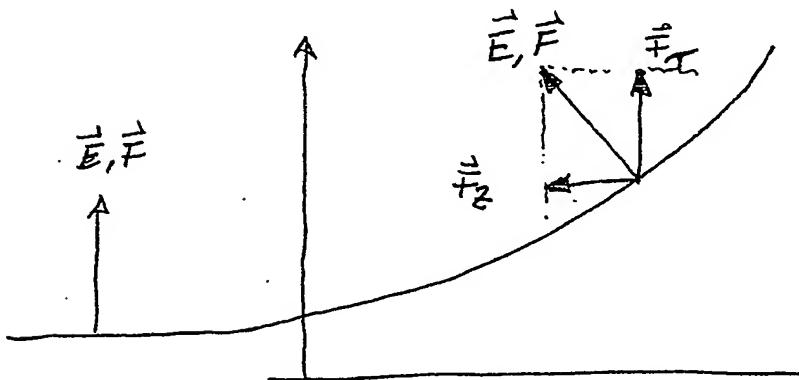
$\vec{E}, \vec{F}$ $\vec{F}_{\tau}$

$\vec{F}_{z}$

$\vec{E}, \vec{F}$

FIG. 1g.

PRIOR ART

Rh
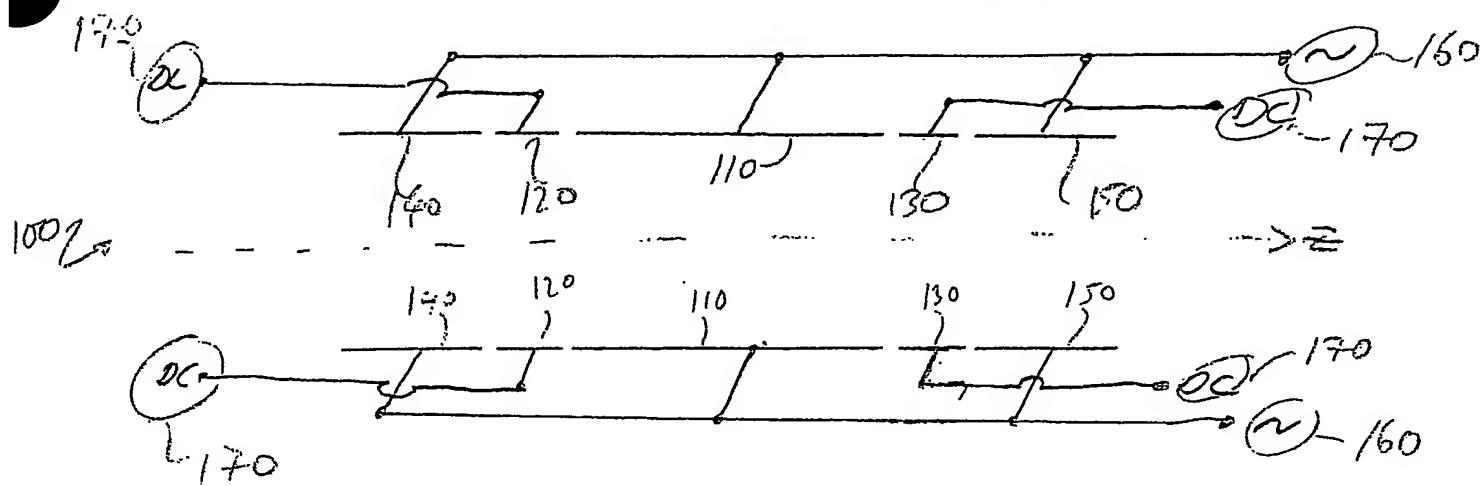
Fig. 2a

Storage field:

$\vec{B}$ homogeneous
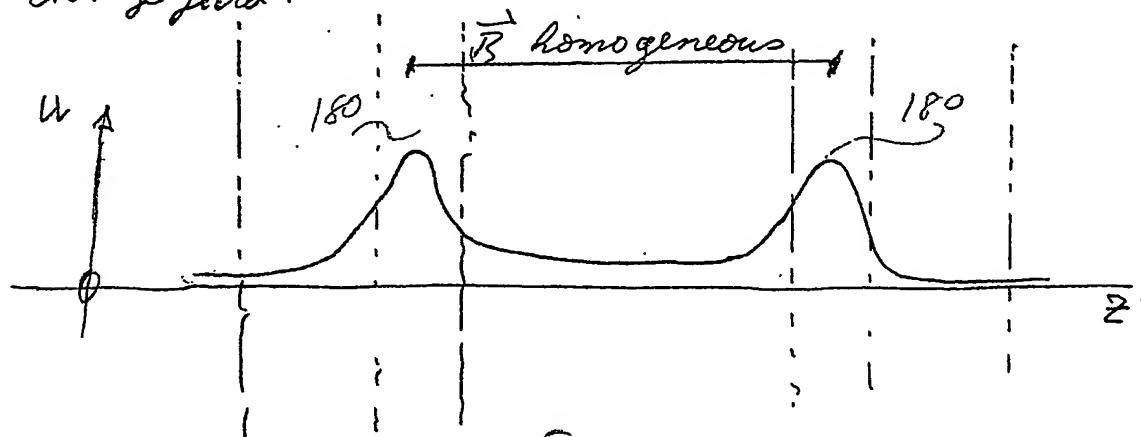
Fig. 2b.

Excitation field: isopotential lines

Fig 2c

region of confinement
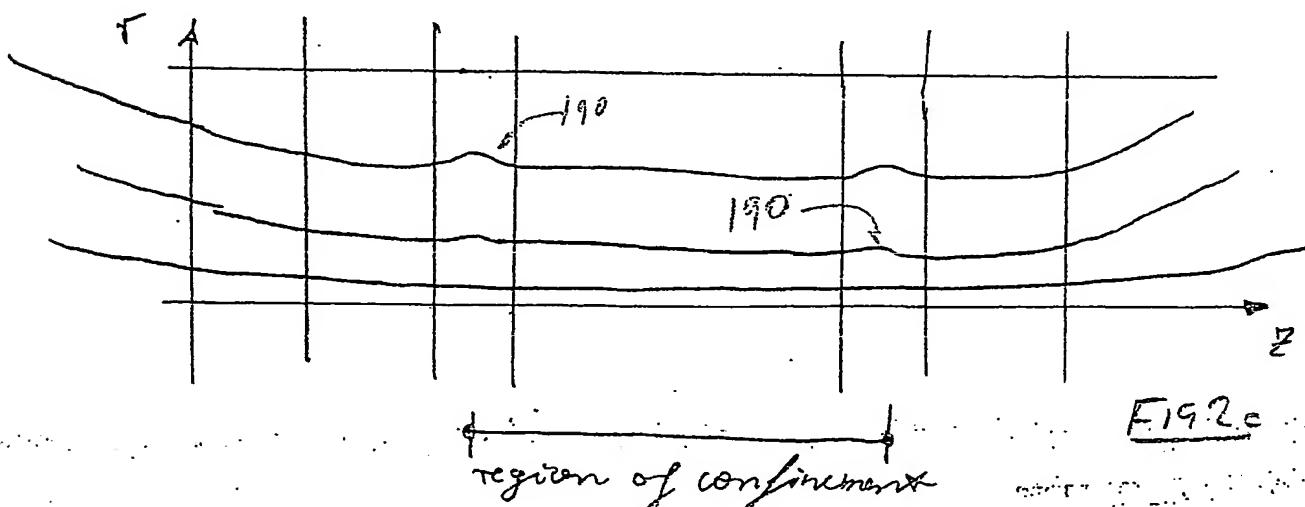
Segments; excitation on all electrodes

RF   RF+DC   RF   RF+DC RF

$\overset{\text{logical}}{}$

| 140 | 120 | 110 | 130 | 150 |

→ z

DC 170

200   200

→ DC

possible wiring

~.RF

Fig 3a   160

Excitation field : isopotential lines

physical cell dimensions

→ z

region of confinement

Fig 3b
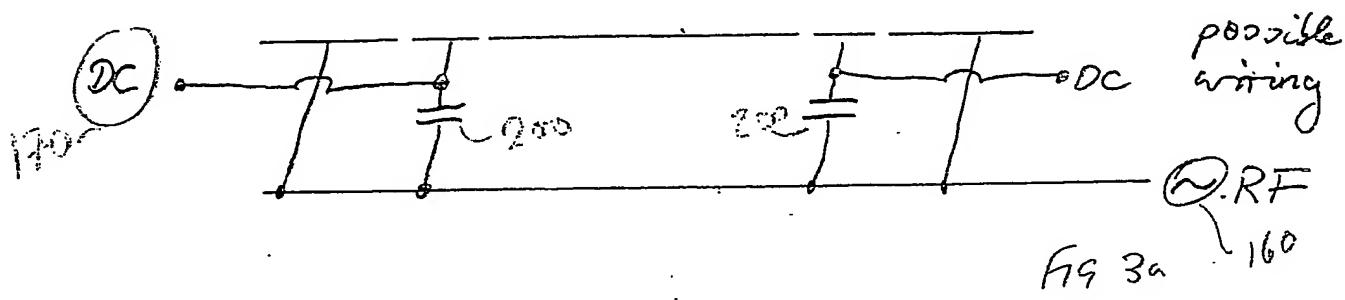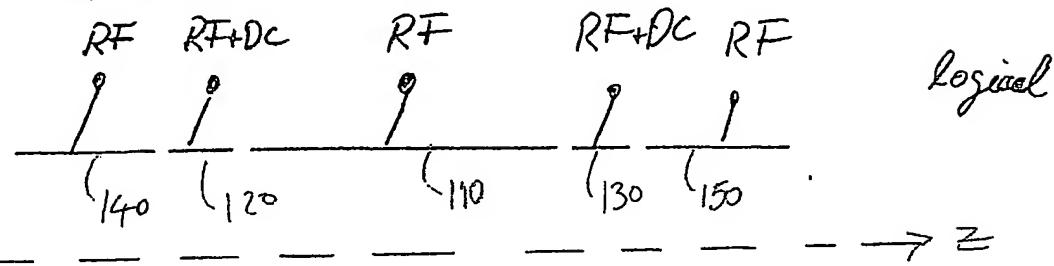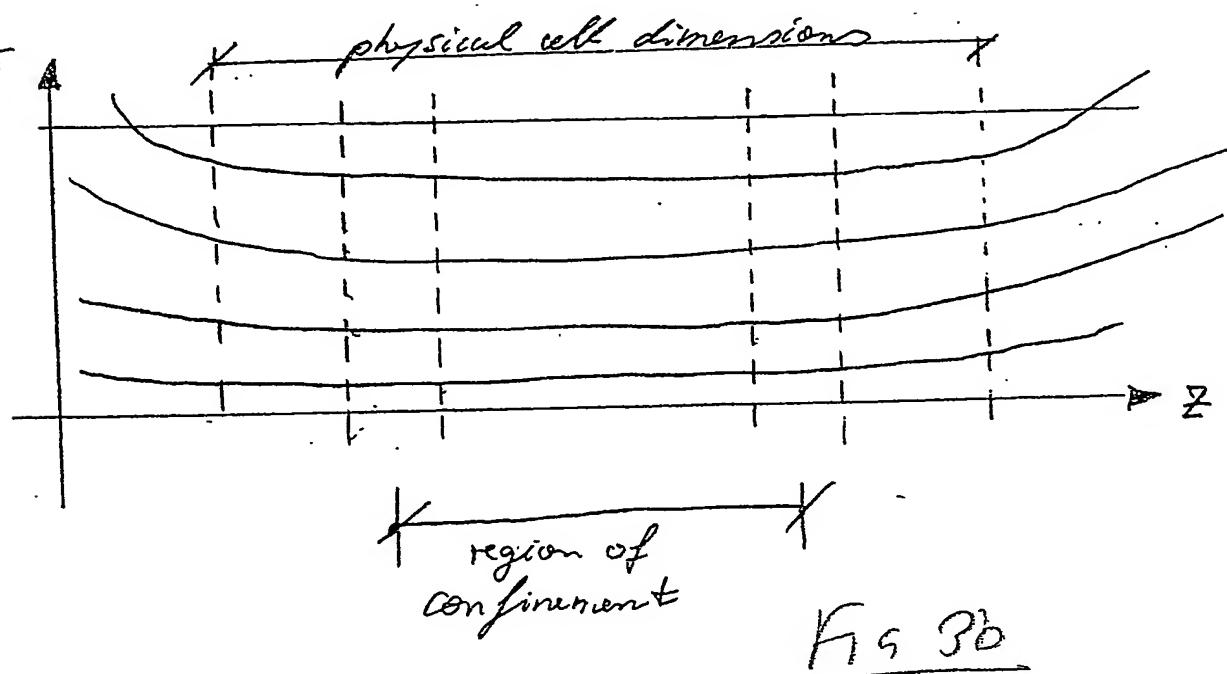
most flexible application:

RF DC RF DC RF DC RF DC RF DC logical assignment

$100''$

(140 (120 (10 (130 (150

— — — — — — — — — — — — Z

DC_5 — — DC_4 — DC_3 — DC_2 — DC_1 possible wiring

200

∼ RF
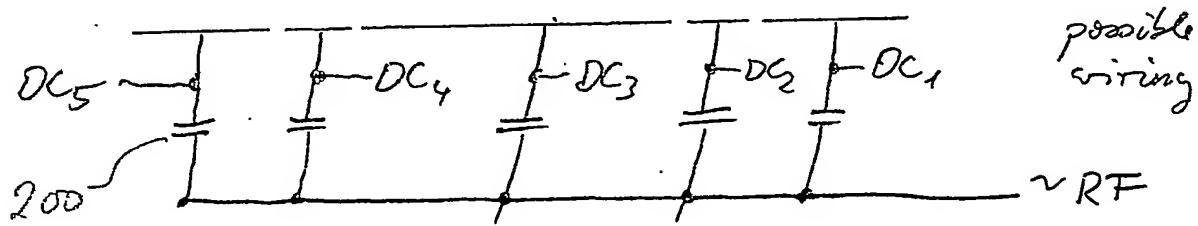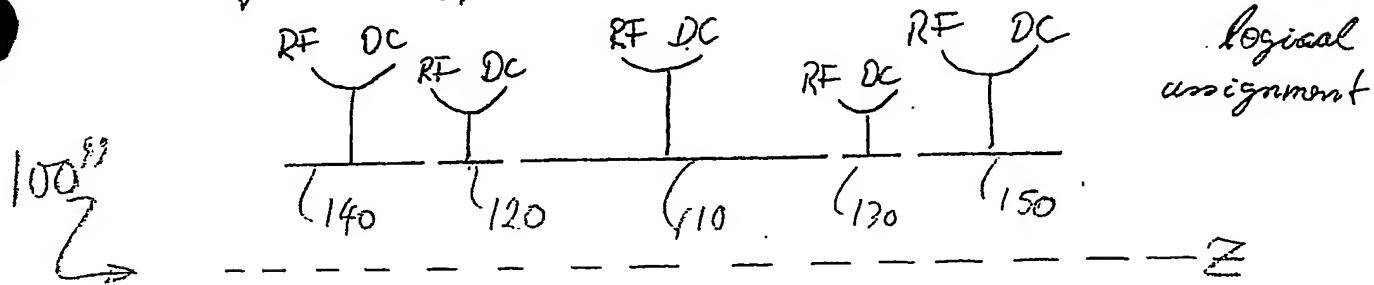
allows various static field combinations,
depending on use.

FIG 4

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2003